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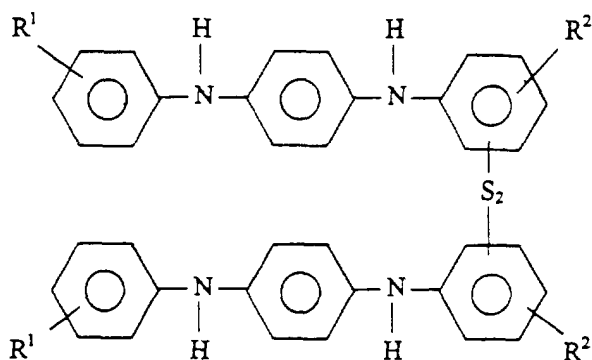
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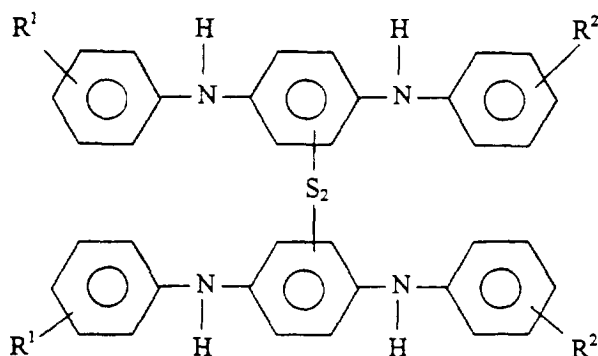
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L-7750 Colmar-Berg (LU)(54) **Diaryl-p-phenylenediamine disulfides**

(57) The present invention relates to mixed diaryl-p-phenylenediamine disulfides and its use in compounds. The mixed diaryl-p-phenylenediamine are of the formula

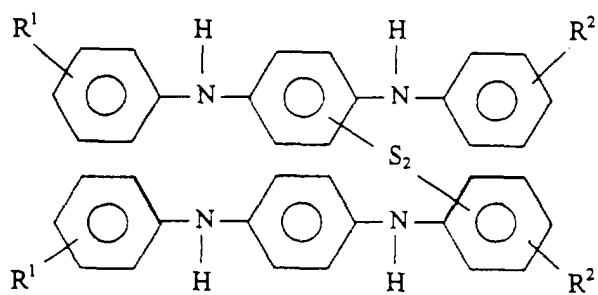


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III

and mixtures thereof wherein R^1 and R^2 are each independently selected from the group consisting of hydrogen and alkyls having from 1 to 8 carbon atoms.

Description

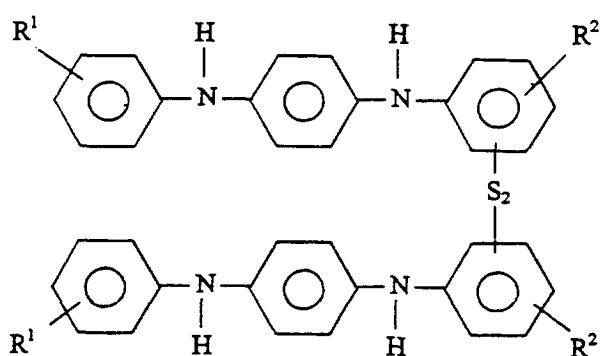
Background of the Invention

[0001] Conventional N-aryl substituted diphenyldiamine antioxidants, such as Wingstay® 100 are widely used in the protection of rubber. Wingstay® 100 is commercially available from The Goodyear Tire & Rubber Company and contains a mixture of di-o-tolyl-p-phenylenediamine, diphenyl-p-phenylenediamine and phenyl-o-tolyl-p-phenylenediamine.

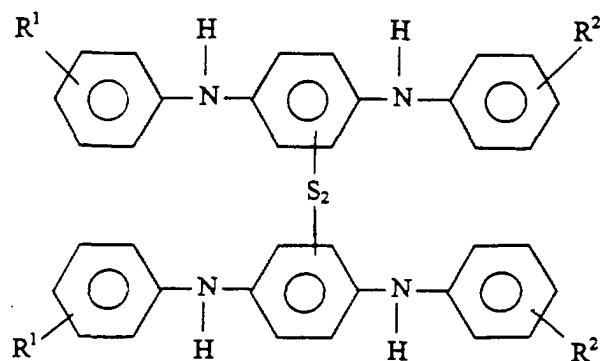
[0002] While use of these conventional N-aryl substituted diphenyldiamine antioxidants provide excellent protection of rubber, improvements to the green strength of rubber is not observed. In order to obtain improvements to green strength, expensive crosslinkers are conventionally used. Unfortunately, use of such crosslinkers significantly increase the cost of production of such rubber compounds.

Summary of the Invention

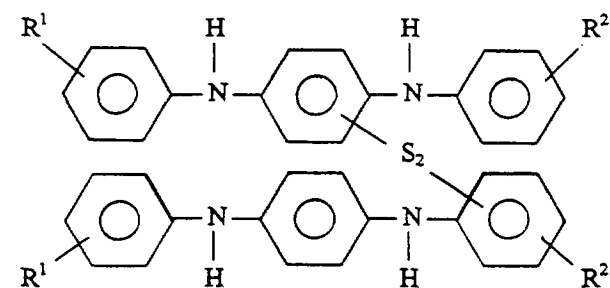
[0003] The present invention relates diaryl-p-phenylenediamine disulfides of the formula:



I



II

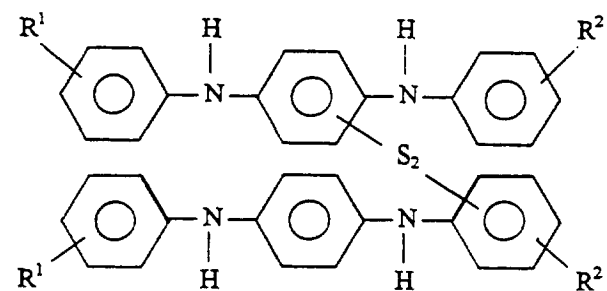
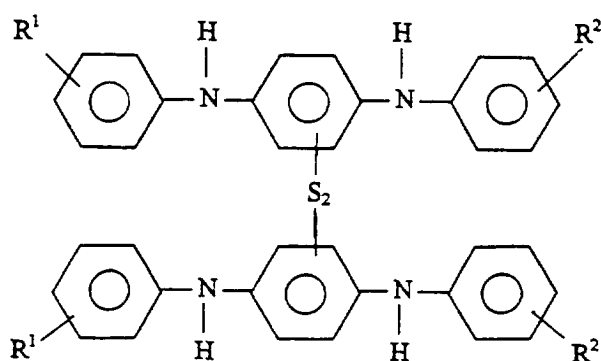
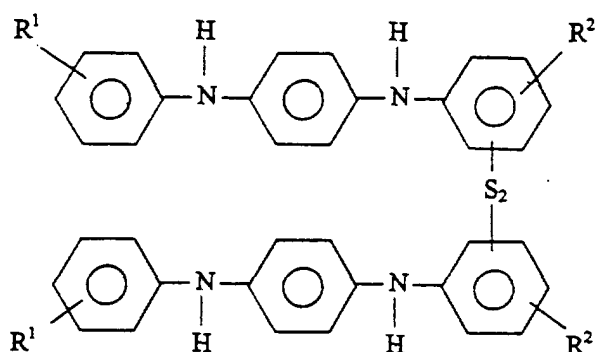


III

and mixtures thereof, wherein R¹ and R² are each independently selected from the group consisting of hydrogen and alkyls having 1 to 8 carbon atoms.

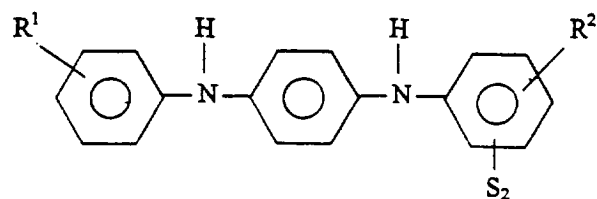
Detailed Description of the Preferred Embodiment

[0004] The present invention also relates to a rubber composition containing from 0.1 to 10 phr of diaryl-p-phenylenediamine disulfides of the formula:

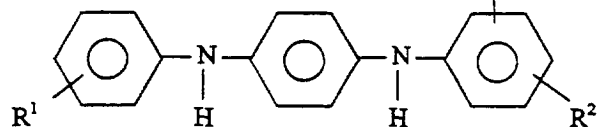


and mixtures thereof, wherein R^1 and R^2 are each independently selected from the group consisting of hydrogen and alkyls having 1 to 8 carbon atoms.

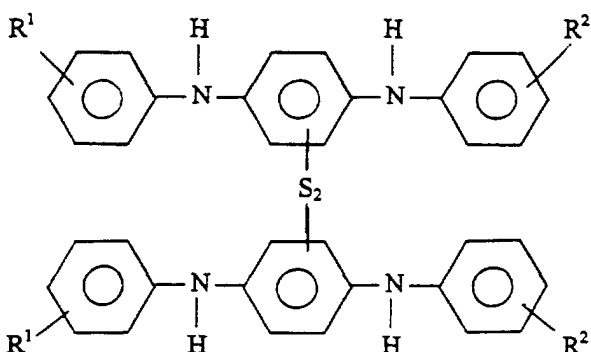
[0005] In addition, there is disclosed a method for processing rubber comprising mixing with a rubber from 0.1 to 10 phr of a diaryl-p-phenylenediamine disulfides of the formula:



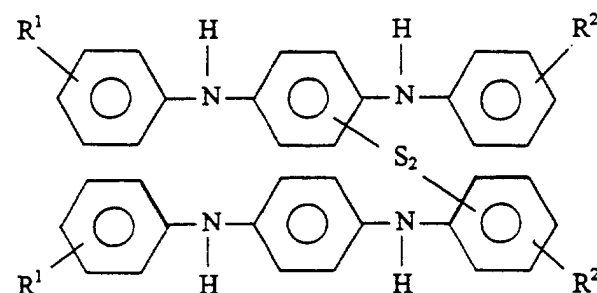
I



II



III

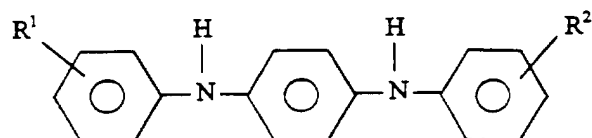


IV

and mixtures thereof, wherein R^1 and R^2 are each independently selected from the group consisting of hydrogen and alkyls having 1 to 8 carbon atoms.

[0006] The disulfides used in the present invention may be present at various levels in the rubber compounds of the present invention. For example, the level may range from about 0.1 to 10.0 parts by weight per 100 parts by weight of rubber (also known as "phr"). Preferably, the level ranges from about 0.5 to about 5.0 phr.

[0007] The disulfides may be prepared by reacting a suitable substituted or unsubstituted diaryl-p-phenylenediamine with a sulfur compound. Representative of suitable diaryl-p-phenylenediamine disulfides compounds which may be used include those of the formula:



[0008] A N-aryl or N-alkaryl substituted diphenyldiamine of the above formula is used to prepare the disulfide compositions of the present invention. With respect to the above formula, each R^1 and R^2 may consist of hydrogen or an alkyl having a total of from about 1 to about 8 carbon atoms. R^1 and R^2 , however, may be different from the other substituent. Preferably, R^1 and R^2 are each hydrogen or an alkyl having 1 to 3 carbons. Representative of N-aryl

substituted and N-alkaryl substituted diphenyldiamines which may be suitable for use in preparation of the compositions of the present invention include diphenyl-p-phenylenediamine, di-o-tolyl-p-phenylenediamine, phenyl-o-tolyl-p-phenylenediamine, di-o-xylyl-p-phenylenediamine, phenyl-o-xylyl-p-phenylenediamine, di-m-tolyl-p-phenylenediamine, phenyl-m-tolyl-p-phenylenediamine, di-m-xylyl-p-phenylenediamine, phenyl-m-xylyl-p-phenylenediamine, di-o-isopropylphenyl-p-phenylenediamine, phenyl-o-isopropylphenyl-p-phenylenediamine to name a few. The most preferred N-aryl substituted and N-alkaryl substituted diphenyldiamine is a mixture di-o-tolyl-p-phenylenediamine, diphenyl-p-phenylenediamine and phenyl-o-tolyl-p-phenylenediamine known in the industry as Wingstay® 100.

[0009] Representative examples of sulfur compounds which may be used include sulfur monochloride and sulfur dichloride. Preferably, the sulfur compound is sulfur monochloride.

[0010] The diaryl-p-phenylenediamine of formula IV is reacted with a sulfur compound under suitable conditions to form a disulfide of the formulas I, II and/or III. The diaryl-p-phenylenediamine may be reacted with sulfur in a variety of mole ratios. Generally, the mole ratio of the diaryl-p-phenylenediamine to the sulfur compound ranges from about 1.0:0.5 to about 1.0:10.0 with a range of from about 1.0:6.0 to about 1.0:2.0 being preferred.

[0011] Since the sulfur compound is halogenated, such as sulfur monochloride, it is preferred to conduct the reaction between the sulfur compound and the diaryl-p-phenylenediamine in the presence of a scavenger or "neutralizer" which does not interfere with the disulfide formation. Representative examples include triethylamine, pyridines such as methyl pyridine and the like.

[0012] An organic solvent may be used to dissolve the diaryl-p-phenylenediamine compound. The solvent is preferably inert to the reaction between the diaryl-p-phenylenediamine and the sulfur compound. Illustrative of solvents suitable for use in the practice of this invention include: saturated and aromatic hydrocarbons, e.g., hexane, octane, dodecane, naphtha, decalin, tetrahydronaphthalene, kerosene, mineral oil, cyclohexane, cycloheptane, alkyl cycloalkane, benzene, toluene, xylene, alkylnaphthalene, and the like; acetone; ethers such as tetrahydrofuran, tetrahydropyran, diethylether, 1,2-dimethoxybenzene, 1,2-diethoxybenzene, the dialkylethers of ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, oxyethyleneoxypropylene glycol, and the like; fluorinated hydrocarbons that are inert under the reaction conditions such as perfluoroethane, monofluorobenzene, and the like. Another class of solvents are sulfones such as dimethylsulfone, diethylsulfone, diphenolsulfone, sulfolane, and the like. Mixtures of the aforementioned solvents may be employed so long as they are compatible with each other under the conditions of the reaction and will adequately dissolve the diaryl-p-phenylenediamine compound and not interfere with the reaction.

[0013] The reaction between the diaryl-p-phenylenediamine and the sulfur compound to form the diaryl-p-phenylenediamine disulfides is exothermic and may be conducted over a wide temperature range. The temperature may range from moderate to an elevated temperature. In general, the reaction may be conducted at a temperature of between about 0°C to 150°C. The preferred temperature range is from about 50°C to 120°C, while the most preferred temperature range is from about 80°C to 100°C.

[0014] The reaction pressure to form the diaryl-p-phenylenediamine disulfide is not deemed to be critical. Pressures ranging from about 0 kPa to 689 kPa may be used.

[0015] The reaction is preferably conducted in a nitrogen atmosphere.

[0016] The process for the preparation of the diaryl-p-phenylenediamine disulfide may be carried out in a batch, semi-continuous or continuous manner. The reaction may be conducted in a single reaction zone or in a plurality or reaction zones, in series or in parallel. The reaction may be conducted intermittently or continuously in an elongated tubular zone or in a series of such zones. The material of construction of the equipment should be such as to be inert during the reaction. The equipment should also be able to withstand the reaction temperatures and pressures. The reaction zone can be fitted with internal and/or external heat exchangers to control temperature fluctuations. Preferably, an agitation means is available to ensure the uniform reaction. Mixing induced by vibration, shaker, stirrer, rotating, oscillation, etc. are all illustrative of the types of agitation means which are contemplated for use in preparing the composition of the present invention. Such agitation means are available and well known to those skilled in the art.

[0017] The diaryl-p-phenylenediamine disulfides may be used in "elastomers or rubbers." The term "elastomer or rubber" as used herein embraces both vulcanized forms of natural and all its various raw and reclaim forms as well as various synthetic rubbers. The synthetic elastomers include conjugated diene homopolymers and copolymers and copolymers of at least one conjugated diene and aromatic vinyl compound. Representative synthetic polymers include the homopolymerization products of butadiene and its homologues and derivatives, as for example, methyl-butadiene, dimethylbutadiene and pentadiene as well as copolymers, such as those formed from butadiene or its homologues or derivatives with other unsaturated organic compounds. Among the latter are acetylenes, for example, vinyl acetylene; olefins, for example, isobutylene, which copolymerizes with isoprene to form butyl rubber; vinyl compounds, for example, acrylic acid, acrylonitrile (which polymerizes with butadiene to form NBR), methacrylic acid and styrene, the latter polymerizing with butadiene to form SBR, as well as vinyl esters and various unsaturated aldehydes, ketones and ethers, e.g. acrolein, methyl isopropenyl ketone and vinyl ethyl ether. Also included are the various synthetic rubbers prepared by the homopolymerization of isoprene and the copolymerization of isoprene and other diolefins in various unsaturated organic compounds. Also included are the synthetic rubbers such as 1,4-cis-polybutadiene and 1,4-cis-

polyisoprene and similar synthetic rubbers.

[0018] Specific examples of synthetic rubbers include neoprene (polychloroprene), polybutadiene (including trans- and cis-1,4-polybutadiene), polyisoprene (including cis-1,4-polyisoprene), butyl rubber, copolymers of 1,3-butadiene or isoprene with monomers such as styrene, acrylonitrile and methyl methacrylate as well as ethylene/propylene terpolymers, also known as ethylene/propylene/diene monomer (EPDM) and, in particular, ethylene/propylene/dicyclopentadiene terpolymers and styrene/isoprene/butadiene rubber. The preferred synthetic rubbers for use in the present invention are polybutadiene, butadiene-styrene copolymers and cis,1,4-polyisoprene.

[0019] Vulcanization of the rubber compound of the present invention is generally carried out at conventional temperatures ranging from about 100°C and 200°C. Preferably, the vulcanization is conducted at temperatures ranging from about 110°C to 180°C. Any of the usual vulcanization processes may be used such as heating in a press or mold, heating with superheated steam or hot air or in a salt bath.

[0020] In addition to the diaryl-p-phenylenediamine disulfide, other rubber additives may also be incorporated in the rubber compound. The additives commonly used in rubber vulcanizates are, for example, carbon black, tackifier resins, processing aids, antioxidants, antiozonants, stearic acid, activators, waxes, phenol-formaldehyde resins, oils and peptizing agents. As known to those skilled in the art, depending on the intended use of the rubber compound, certain additives mentioned above are commonly used in conventional amounts. Typical additions of carbon black comprise about 20 to 100 parts by weight per 100 parts by weight of rubber (phr), preferably 30 to 80 phr. Typical amounts of tackifier resins comprise about 1 to 5 phr. Typical amounts of antioxidants comprise 1 to about 10 phr. Typical amounts of antiozonants comprise 1 to about 10 phr. Typical amounts of stearic acid comprise 1 to about 2 phr. Typical amounts of zinc oxide comprise 2 to 5 phr. Typical amounts of waxes comprise 1 to 5 phr. Typical amounts of phenol-formaldehyde resins comprise 1 to 8 phr. Typical amounts of oils comprise 5 to 40 phr. Typical amounts of peptizers comprise 0.1 to 1 phr. The presence and relative amounts of the above additives are not an aspect of the present invention.

[0021] The rubber composition may contain a silica filler. The silica filler may be added in amounts ranging from 10 to 250 phr. Preferably, the silica is present in an amount ranging from 15 to 80 phr.

[0022] The commonly employed particulate precipitated silica used in rubber compounding applications can be used as the silica in this invention. These precipitated silicas include, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate.

[0023] Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304 (1930).

[0024] The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300.

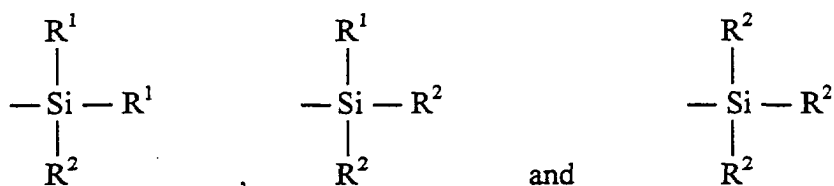
[0025] The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

[0026] Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the HiSil trademark with designations 210, 243, etc; silicas available from Rhodia, with, for example, designations of Z1165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2 and VN3, etc.

[0027] In those instances where diaryl-p-phenylenediamine disulfides are added to a silica-filled rubber composition, the processing of the sulfur vulcanizable rubber may be conducted in the presence of a sulfur containing organosilicon compound. Examples of suitable sulfur containing organosilicon compounds are of the formula:



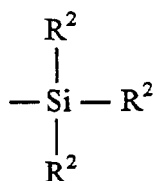
in which Z is selected from the group consisting of



where R¹ is an alkyl group of 1 to 4 carbon atoms, cyclohexyl or phenyl; R² is alkoxy of 1 to 8 carbon atoms, or cycloalkoxy of 5 to 8 carbon atoms; Alk is a divalent hydrocarbon of 1 to 18 carbon atoms and n is an integer of 2 to 8.

[0028] Specific examples of sulfur containing organosilicon compounds which may be used in accordance with the present invention include: 3,3'-bis(trimethoxysilylpropyl) disulfide, 3,3'-bis(triethoxysilylpropyl) tetrasulfide, 3,3'-bis(triethoxysilylpropyl) octasulfide, 3,3'-bis(trimethoxysilylpropyl) tetrasulfide, 2,2'-bis(triethoxysilylethyl) tetrasulfide, 3,3'-bis(trimethoxysilylpropyl) trisulfide, 3,3'-bis(triethoxysilylpropyl) trisulfide, 3,3'-bis(tributoxysilylpropyl) disulfide, 3,3'-bis(trimethoxysilylpropyl) hexasulfide, 3,3'-bis(trimethoxysilylpropyl) octasulfide, 3,3'-bis(trioctoxysilylpropyl) tetrasulfide, 3,3'-bis(trihexoxysilylpropyl) disulfide, 3,3'-bis(tri-2-ethylhexoxysilylpropyl) trisulfide, 3,3'-bis(triisooctoxysilylpropyl) tetrasulfide, 3,3'-bis(tri-t-butoxysilylpropyl) disulfide, 2,2'-bis(methoxy diethoxy silyl ethyl) tetrasulfide, 2,2'-bis(tripropoxysilylethyl) pentasulfide, 3,3'-bis(tricyclohexoxysilylpropyl) tetrasulfide, 3,3'-bis(tricyclopentoxysilylpropyl) trisulfide, 2,2'-bis(tri-2-methylcyclohexoxysilylethyl) tetrasulfide, bis(trimethoxysilylmethyl) tetrasulfide, 3-methoxy ethoxy propoxysilyl 3'-diethoxybutoxy-silylpropyltetrasulfide, 2,2'-bis(dimethyl methoxysilylethyl) disulfide, 2,2'-bis(dimethyl sec. butoxysilylethyl) trisulfide, 3,3'-bis(methyl butylethoxysilylpropyl) tetrasulfide, 3,3'-bis(di t-butylmethoxysilylpropyl) tetrasulfide, 2,2'-bis(phenyl methyl methoxysilylethyl) trisulfide, 3,3'-bis(diphenyl isopropoxysilylpropyl) tetrasulfide, 3,3'-bis(diphenyl cyclohexoxysilylpropyl) disulfide, 3,3'-bis(dimethyl ethylmercaptosilylpropyl) tetrasulfide, 2,2'-bis(methyl dimethoxysilylethyl) trisulfide, 2,2'-bis(methyl ethoxypropoxysilylethyl) tetrasulfide, 3,3'-bis(diethyl methoxysilylpropyl) tetrasulfide, 3,3'-bis(ethyl di-sec. butoxysilylpropyl) disulfide, 3,3'-bis(propyl diethoxysilylpropyl) disulfide, 3,3'-bis(butyl dimethoxysilylpropyl) trisulfide, 3,3'-bis(phenyl dimethoxysilylpropyl) tetrasulfide, 3-phenyl ethoxybutoxysilyl 3'-trimethoxysilylpropyl tetrasulfide, 4,4'-bis(trimethoxysilylbutyl) tetrasulfide, 6,6'-bis(triethoxysilylhexyl) tetrasulfide, 12,12'-bis(triisopropoxysilyl dodecyl) disulfide, 18,18'-bis(trimethoxysilyloctadecyl) tetrasulfide, 18,18'-bis(tripropoxysilyloctadecyl) tetrasulfide, 4,4'-bis(trimethoxysilylbuten-2-yl) tetrasulfide, 4,4'-bis(trimethoxysilylcyclohexylene) tetrasulfide, 5,5'-bis(dimethoxymethylsilylpentyl) trisulfide, 3,3'-bis(trimethoxysilyl-2-methylpropyl) tetrasulfide, 3,3'-bis(dimethoxyphenylsilyl-2-methylpropyl) disulfide.

[0029] The preferred sulfur containing organosilicon compounds are the 3,3'-bis(trimethoxy or triethoxy silylpropyl) sulfides. The most preferred compound is 3,3'-bis(triethoxysilylpropyl) tetrasulfide. Therefore as to formula V, preferably Z is



where R² is an alkoxy of 2 to 4 carbon atoms, with 2 carbon atoms being particularly preferred; Alk is a divalent hydrocarbon of 2 to 4 carbon atoms with 3 carbon atoms being particularly preferred; and n is an integer of from 2 to 5 with 4 being particularly preferred.

[0030] The amount of the sulfur containing organosilicon compound of formula V in a rubber composition will vary depending on the level of silica that is used. Generally speaking, the amount of the compound of formula V, if used, will range from .01 to 1.0 parts by weight per part by weight of the silica. Preferably, the amount will range from .05 to 0.4 parts by weight per part by weight of the silica.

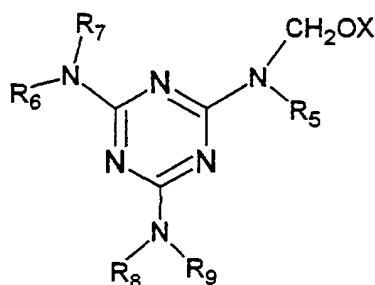
[0031] The vulcanization of the rubber compound is conducted in the presence of a sulfur-vulcanizing agent. Examples of suitable sulfur-vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur-vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur-vulcanizing agents are used in an amount ranging from about 0.5 to 8 phr with a range of from 1.0 to 2.25 being preferred.

[0032] Accelerators are conventionally used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In some instances, a single accelerator system may be used, i.e., primary accelerator. Conventionally, a primary accelerator is used in amounts ranging from about 0.5 to 2.0 phr. In another instance, combinations of two or more accelerators may be used which may consist of a primary accelerator which is generally used in the large amount (0.5 to 2.0 phr), and a secondary accelerator which is generally used in smaller amounts (0.01 to 0.50 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators have been known to produce a synergistic effect of the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce satisfactory cures at ordinary vulcanization temperatures. Suitable types of accelerators that may be used include amines, disulfides, guanidines, thiophthalimides, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfena-

mide. If a secondary accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

[0033] The rubber compound may also contain a cure activator. A representative cure activator is methyl trialkyl (C_8-C_{10}) ammonium chloride, commercially available under the trademark Adogen from Sherex Chemical of Dublin, Ohio. The amount of activator may range from 0.05 phr to 5 phr.

[0034] The rubber compositions of the present invention may contain a methylene donor and a methylene acceptor. The term "methylene donor" is intended to mean a compound capable of reacting with a methylene acceptor (such as resorcinol or its equivalent containing a present hydroxyl group) and generate the resin in-situ. Examples of methylene donors which are suitable for use in the present invention include hexamethylenetetramine, hexaethoxymethylmelamine, hexamethoxymethylmelamine, lauryloxymethylpyridinium chloride, ethoxymethylpyridinium chloride, trioxan hexamethoxymethylmelamine, the hydroxy groups of which may be esterified or partly esterified, and polymers of formaldehyde such as paraformaldehyde. In addition, the ethylene donors may be N-substituted oxymethylmelamines, of the general formula:



wherein X is an alkyl having from 1 to 8 carbon atoms, R^5 , R^6 , R^7 , R^8 and R^9 are individually selected from the group consisting of hydrogen, an alkyl having from 1 to 8 carbon atoms and the group $-CH_2OX$. Specific methylene donors include hexakis-methoxymethyl)melamine, N,N',N"-trimethyl/N,N',N"-trimethylolmelamine, hexamethylolmelamine, N,N',N"-dimethylolmelamine, N-methylolmelamine, N,N'-dimethylolmelamine, N,N',N"-tris(methoxymethyl)melamine and N,N',N"-tributyl-N,N',N"-trimethylol-melamine. The N-methylol derivatives of melamine are prepared by known methods.

[0035] The amount of methylene donor and methylene acceptor that is present in the rubber stock may vary. Typically, the amount of methylene donor and methylene acceptor that each is present will range from about 0.1 phr to 10.0 phr. Preferably, the amount of methylene donor and methylene acceptor that each is present ranges from about 2.0 phr to 5.0 phr.

[0036] The weight ratio of methylene donor to the methylene acceptor may vary. Generally speaking, the weight ratio will range from about 1:10 to about 10:1. Preferably, the weight ratio ranges from about 1:3 to 3:1.

[0037] The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example the ingredients are typically mixed in at least two stages, namely at least one non-productive stage followed by a productive mix stage. The final curatives including sulfur vulcanizing agents are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber and disulfide of formulas I and III are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art. The rubber composition containing at least part of the silica and the sulfur-containing organosilicon compound should be subjected to a thermomechanical mixing step. The thermomechanical mixing step generally comprises a mechanical working in a mixer or extruder for a period of time suitable in order to produce a rubber temperature between $140^{\circ}C$ and $190^{\circ}C$. The appropriate duration of the thermomechanical working varies as a function of the operating conditions and the volume and nature of the components. For example, the thermomechanical working may be from 1 to 20 minutes.

[0038] Vulcanization of the rubber composition of the present invention is generally carried out at conventional temperatures ranging from about $100^{\circ}C$ to $200^{\circ}C$. Preferably, the vulcanization is conducted at temperatures ranging from about $110^{\circ}C$ to $180^{\circ}C$. Any of the usual vulcanization processes may be used such as heating in a press or mold, heating with superheated steam or hot air or in a salt bath.

[0039] The rubber compounds containing the diaryl-p-phenylenediamine disulfides may be used in the preparation of and, therefore, in the form of composite products including tires, power belts, conveyor belts, printing rolls, rubber shoe heels and soles, rubber wringers, automobile floor mats, mud flaps for trucks, ball mill liners, and the like. Preferably, the rubber vulcanizates are used in sidewall, tread, carcass ply, wirecoat or overlay compounds for tires.

[0040] The following examples are presented in order to illustrate but not limit the present invention.

[0041] Cure properties were determined using a Monsanto oscillating disc rheometer which was operated at a temperature of 150°C and at a frequency of 11 hertz. A description of oscillating disc rheometers can be found in the Vanderbilt Rubber Handbook edited by Robert O. Ohm (Norwalk, Conn., R. T. Vanderbilt Company, Inc., 1990), Pages 554 through 557. The use of this cure meter and standardized values read from the curve are specified in ASTM D-2084. A typical cure curve obtained on an oscillating disc rheometer is shown on Page 555 of the 1990 edition of the Vanderbilt Rubber Handbook.

[0042] In such an oscillating disc rheometer, compounded rubber samples are subjected to an oscillating shearing action of constant amplitude. The torque of the oscillating disc embedded in the stock that is being tested that is required to oscillate the rotor at the vulcanization temperature is measured. The values obtained using this cure test are very significant since changes in the rubber or the compounding recipe are very readily detected.

[0043] The following tables report cure properties that were determined from cure curves that were obtained for the three rubber formulations that were prepared. These properties include torque maximum (Tmax), torque minimum (Tmin), delta torque (DEL T), minutes to 1 point of the torque increase (T1) and minutes to 90 percent of the torque increase (T90). Green strength was determined by ASTM D-412 using an uncured sample. The sample is molded at a temperature below the cure temperature.

Example 1

Preparation of Diaryl-p-phenylenediamine Disulfide

[0044] A 2-liter, round-bottom flask was charged with 54.8 g (0.2 mole) of Wingstay® 100 in 250 ml of dry toluene. The solution was stirred under nitrogen as 13.5 g (0.1 mole) of sulfur monochloride was added dropwise. The reaction mixture exotherm increased the temperature to about 44°C with an addition time of about 20 minutes. The reaction mixture was heated to 95°C for an additional 40 minutes with stirring. The mixture was treated with 250 ml of toluene with stirring and then with 500 ml of water and 200 g of NaCl, stirred and phase-separated. The organic layer was stripped of volatiles to give 62 g of a dark disulfide crystals melting at 81 to 89°C. Small molecule GPC analysis and NMR analysis shows coupling and the sulfur analysis shows 10.2 to 10.5 percent sulfur.

Example 2

Physical Testing

[0045] Table I below shows the basic rubber compound that was used in this example. The rubber compound was prepared in a two-stage Banbury mix. All parts and percentages are by weight unless otherwise noted. All samples were prepared with the same procedure and ingredients except as to the use of the respective amount (phr) of ingredients listed in Table II. The cure data as well as other physical data for each sample are listed in Table II. In Table II, the various properties are reported for samples which were cured for 27 minutes at 150°C.

Table I

Non-productive 1	(phr)
Natural rubber	100.0
Carbon black	50
Disulfide of Example 1	Varied
Zinc oxide	5.0
Stearic acid	2.0
Processing oil	5.0
Productive	
Sulfur	1.4
Accelerator ¹	0.8

¹N-tert-butyl-2-benzothiazole sulfenamide

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Table II

	Control Sample 1	Sample 2	Sample 3
Disulfide of Example 1	0	3	5
Rheometer, 150°C			
Maximum torque	38.6	39.3	40.6
Minimum torque	8.3	9.6	10
Delta torque	30.3	29.7	30.6
T90(min.)	12.3	10	9
T 25 (min.)	8.8	6.5	5.3
Rev, 60	1	1.3	1.5
Tensile strength (MPa)	24	26	22.9
Elongation at break (%)	553	548	542
Modulus			
100%	2.12	2.31	2.39
300%	11.4	11.7	11.7
Rebound			
Room temperature	47.5	46.6	46.4
100°C	63.3	60.8	59.8
Hardness			
Room temperature	63.5	60.8	59.8
100°C	57.4	59.2	61.1
Streblor, 95°C (Newtons)	142	137	135
E' at 60°C (MPa)	16.1	19.2	20.5
Tan delta	0.082	0.08	0.07
DIN Abrasion	113	120	127
Seat nylon (Newtons)	103	91	101
Seat polyester (Newtons)	109	94	106
Seat Flexten (Newtons)	103	150	160
Green strength			
40% (MPa)	0.23	0.26	0.25
80% (MPa)	0.33	0.34	0.31
120% (MPa)	0.32	0.34	0.31
480% (MPa)	0.21	0.26	0.25
Tensile at break (MPa)	0.2	0.33	0.46
Elongation at break (%)	633	1270	1442

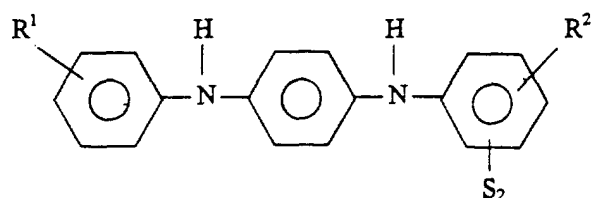
[0046] The above results show that, with the presence of the diaryl-p-phenylenediamine disulfide, the green strength of the compounds were improved. In addition, improvements to Flexten® tire cord adhesion were observed.

[0047] While certain representative embodiment and details have been shown for the purpose of illustrating the

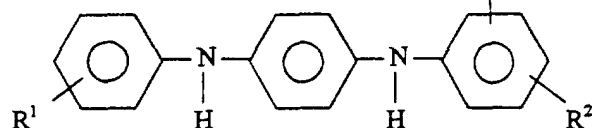
invention, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the spirit

Claims

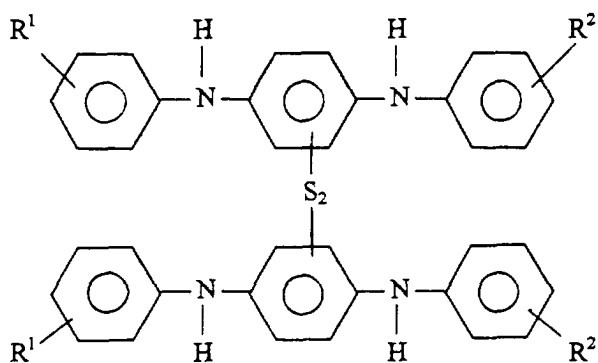
1. A composition **characterized by** a diaryl-p-phenylenediamine disulfide of the formula:



I



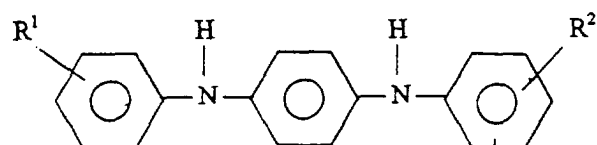
II



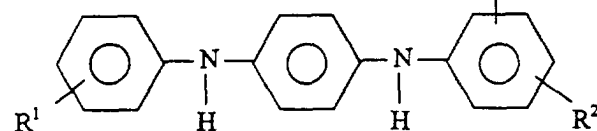
III

and mixtures thereof, wherein R^1 and R^2 are each independently selected from the group consisting of hydrogen and alkyls having 1 to 8 carbon atoms.

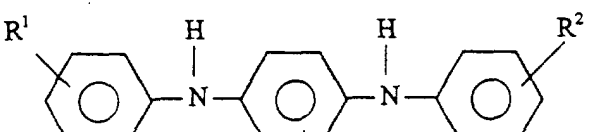
2. A composition **characterized by** a rubber and from 0.1 to 10 phr of a diaryl-p-phenylenediamine disulfides of the formula:



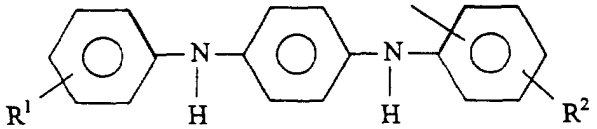
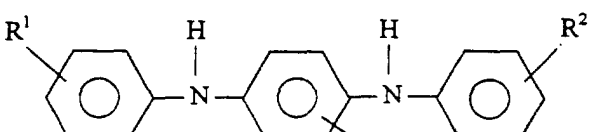
I



II



III



and mixtures thereof, wherein R¹ and R² are each independently selected from the group consisting of hydrogen and alkyls having 1 to 8 carbon atoms.

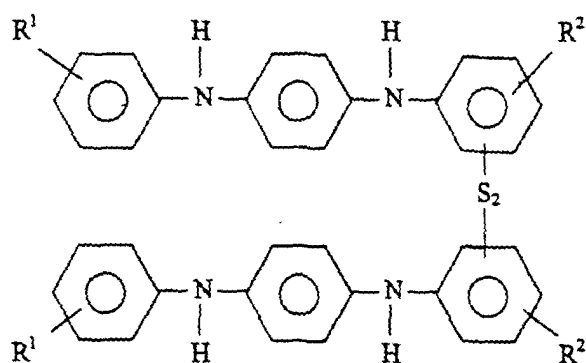
3. The rubber composition of claim 2 **characterized in that** said rubber is selected from the group consisting of a natural rubber and synthetic elastomer selected from conjugated diene homopolymers and copolymers and from copolymers of at least one conjugated diene and aromatic vinyl compound.
4. The rubber composition of claim 3 **characterized in that** said rubber is selected from the group consisting of natural rubber, polychloroprene, synthetic 1,4-cis-polyisoprene, butyl rubber, polybutadiene, styrene-butadiene copolymer, isoprene-butadiene copolymer, styrene-isoprene-butadiene rubber, methyl methacrylate-butadiene copolymer, isoprene-butadiene copolymer, methyl methacrylate-isoprene copolymer, acrylonitrile-isoprene copolymer, acrylonitrile-butadiene copolymer, EPDM and mixtures thereof.
5. The rubber composition of claim 2 **characterized in that** from 0.5 to 5.0 phr of said diaryl-p-phenylenediamine disulfide is present.
6. The rubber composition of claim 2 **characterized by** being in the form of a composite product.

7. The rubber composition of claim 6 **characterized in that** said composite product is selected from the group consisting of tires, power belts, conveyor belts, printing rolls, rubber shoe heels and soles, rubber wringers, automobile floor mats, mud flaps and ball mill liners.

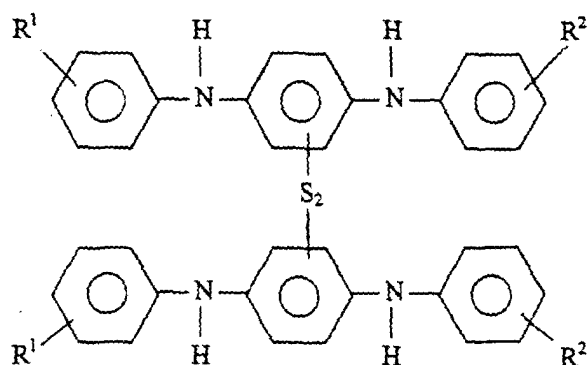
8. The rubber composition of claim 7 **characterized in that** said composite product is a tire.

9. The rubber composition of claim 8 **characterized in that** said rubber composition is used as sidewall, tread carcass ply, wirecoat or overlay compounds.

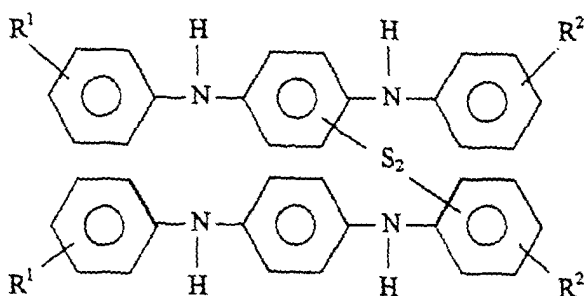
10. A method for processing rubber comprising mixing with a rubber from 0.1 to 10 phr of a diaryl-p-phenylenediamine disulfides of the formula:



I



II



III

and mixtures thereof, wherein R¹ and R² are each independently selected from the group consisting of hydrogen and alkyls having 1 to 8 carbon atoms.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 11 9793

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 939 102 A (GOODYEAR TIRE & RUBBER) 1 September 1999 (1999-09-01) * abstract; claims; examples *	1-10	C07C323/33 C08K5/375 C08K5/372
A	US 3 100 765 A (ALBERT HARRY E) 13 August 1963 (1963-08-13) * claim; examples *	1-10	
A	US 3 057 819 A (KIBLER RICHARD W) 9 October 1962 (1962-10-09) * claims; examples *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08K C07C
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		19 December 2001	Mettler, R-M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background Q : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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19-12-2001

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